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Investigating the composition of dissolved organic matter in natural water in rare earth mine using EEM-PARAFAC analysis

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Abstract

In this study, we have characterized three fluorescent components of dissolved organic matter(DOM) in the surface and underground water of one rare earth elements ore district by excitation-emission matrix fluorescence spectroscopy(EEMs) coupled with parallel factor analysis(PARAFAC). Two protein-like components(C1,tyrosine and C2,trytophan) and one humic-like component(C3) were identified by the DOM Fluor-PARAFAC model, with C3 constituting more than 95% of the total DOM, while C1 and C2 occupying a tiny fraction of DOMs. The distribution of three PARAFAC-identified components was strongly influenced by the river direction, terrain and location of various water samples. The results suggested that DOMs of samples collected from downstream or central region had relatively higher fluorescence intensity than those of upstream or surrounding the center. In addition, a negative linear correlation (R^2=0.8465) between pH (5.7~9.2) and fluorescence intensity of C3 were observed, indicating that the increase of pH might enhance the intensity of fluorescent humic-like substances. Although the fluorescence intensity of C1 and C2 were independent of pH changes, strong quenching effects of different heavy metals were presented for C1, and evident positive correlations between C2 and concentrations of rare earth metals(La, Ce, Tb, Dy, Tm, etc) were observed, which showed that tyrosine-like(C1) and trytophan-like(C2) substances were assumably responsible for metal binding and adsorption in waters, respectively. Based on EEM-PARAFAC modeling, all the fluorescence EEMs of samples could be decomposed into a three-component model, and its potential applications in water quality monitoring and metal-binding indicator were likely to be developed in the fluorescence analysis of natural water.

Keywords: DOM; EEM-PARAFAC; natural water; rare earth mine.

Introduction

Dissolved organic matter(DOM) plays an important role in geochemical processes of surface waters, rivers, oceans, etc. It can combine with metal ions to reduce its bioavailability and biotoxicity to aquatic systems[1,2], meanwhile improving its solubility and ability of transference and translation by binding with organic or inorganic infectants[3]. Currently, dissolved organic matter (DOM) has attracted much attention in biogeochemical research fields due to its importance and the inherent complexity of its chemical composition, chemical structure and multiple sources[4,5,6]. The natural DOM includes a myriad of organic matters, such as humic substances and other biological compounds (e.g., carbohydrates, amino acids and fatty acids)[7,8]. The important component of DOM is humic substances including fulvic acids(FA) and humic acids(HA)[9,10]. Broadly speaking, HA and FA may be classified as special DOM in natural water[11]. Grasso and coworkers[12] postulated that HA and FA make up 25-50% of the total DOM

in natural water, and the remaining DOM has a composition of proteins, polysaccharides and hydrophilic organic acids. The origin, transportation and transformation of DOM may have a direct influence on the recycle and storage ability of carbon in watery environment[13]. So far, the control factors that influence the spatial/temporal distribution are based on qualitative discussions, thus making it very hard to distinguish the comparative impact degree of different controlling factors. Therefore, exploring the different components in DOM of surface and underground water in Jiangxi Mining Area, in the mean time quantitatively analyze DOM of different sources may plays a pivotal role in augmenting our understanding of DOM.

Excitation-emission matrix (EEM) has been widely applied in analyzing the fluorescent properties of DOM in natural watery[14,15,16]. The position of fluorescent peak may qualitatively designate the type and property of the fluorescent matter, and its fluorescent intensity may quantitatively indicate its relative concentration[17]. However, the accurate identification of a fluorescent peak in EEM is usually hampered by the overlap and interference of multiple fluorescent compositions in DOM[18,19]. Besides, this method only determines quite a few peaks in an EEM graph, causing a great quantity of data in experiment unanalyzed when it comes to large sums of samples[20]. In recent years, Stedmon and coworkers[21] have firstly used the parallel factor analysis (PARAFAC) to decipher the EEMs of a DOM fluorescent graph and identified the fluorescent fractions and the corresponding concentrations. The combination of PARAFAC and three-dimensional fluorescent spectrum is also applied in qualitative and quantitative analysis of the multicomponent mixture[22,23]. Since then, PARAFAC has been widely applied in identifying the EEM of soil-extract organic matter[24], continental DOM[25], polluted watery DOM[26], sediment pore-water DOM[27] and ocean water DOM[28].

By PARAFAC modeling, the composition, sources and fate of DOM has been a concern for analysis of samples collected from aquatic environments. Yao[29] determined two humic-like substances and three protein-like components of waterborne DOM from Lake Taihu and its tributaries using PARAFAC model. Yamashita[30]evaluated the spatial distribution of DOM along the coastal zone of the Florida Keys, and determined the regional autochthonous and allochthonous DOM sources. Meng[31] investigated the Zhujiang River by analyzing water samples in an upstream, urbanized area and downstream of the rivers, revealing the presence of tyrosine-like, trytophan-like proteins, humic components, and tracking the origins of DOM in rivers. In addition, the PARAFAC modeling stimulated a broad interest in the study of close connections between DOM and its surroundings. For example, through characterizing PARAFAC-derived DOM components from all titrated samples, the binding of heavy metal with DOM in lake sediments was assessed for further understanding the migration and toxicity of heavy metals[32]. Binding of DOM with heavy metals, especially the rare earth elements, have been widely studied in literatures. Yamamoto[33], Jennifer[34] and Marsac[35] reported the complexation of rare earth elements(REEs) with humic acid at different REE loading levels in aqueous environments. Pourret[36] and Sonke[37] used humic ion-binding model V to analyse REE-humic substances complexation. These previous studies have greatly enhanced our understanding of the formation of REE-humic complexes from the experimental and modeling evidences, but there are still many questions that remain unanswered. A particularly significant one is the determination of dominant components in DOM exhibiting binding behaviors and the correlation between dissolved REE concentrations and fluorescence intensities of DOM in natural waters. Although humic substances are expected to play an important role in binding REEs, it is

still unknown whether other components such as protein-like substances complex with REEs and what elements are more inclined to bound into DOM in natural waters. Such information is needed for a better understanding of the relationship between DOM and REEs studied in a natural REE-rich area. In addition to investigate the distribution and concentration of REEs in soils in rare earth ore district[38,39,40,41], there are few studies on DOM and its correlation with REE along the rivers and tributaries within this area.

The Jiangxi Ore District is an ideal region to study the composition of waterborne DOM because the overexploitation of rare earth metals in the past few years is assumed to have an indispensable impact on the components of DOM due to their strong complexing capacity[42]. Additionally, it is originated from Yangtze River Basin with abundant sunshine and rainfall, as the main stream Tao River runs through the whole area with approximately 55 tributaries spreading over the ore district, which is a typical aquatic environment with balanced water input and runoff and suitable for sample collection. The influence of rare earth metals on natural terrestrial waters could be revealed by the relationship between the concentrations of rare earth metals and the components of DOM of water samples from corresponding area[35]. Our research is to determine the DOM components of natural water by PARAFAC model, and to investigate the distribution trends, various sources for fluorescent DOM, and how the DOM components are related to pH and absorption or complexation of different rare earth metals. The results will be valuable to illustrate the potential of DOM to characterize surface and underground waters in Ore District.

1 Experimental

1.1 Sample Collection

All water samples in this study were collected in the Longnan Ore District, Jiangxi, China in April 2012. These sampling sites were distributed along the main stream and its tributaries spreading over the ore district, which were chosen for China Geological Survey project according to the stationing rules. Samples were collected in clean glass bottles and delivered to the lab under cooled conditions (4°C in cooling boxes) within 48 hours. The samples were then filtered through 0.45 μm Supor filter membranes (Pall, USA) within 24 hours and stored in the dark at 4°C until analysis within two days to minimize bacterial decomposition.

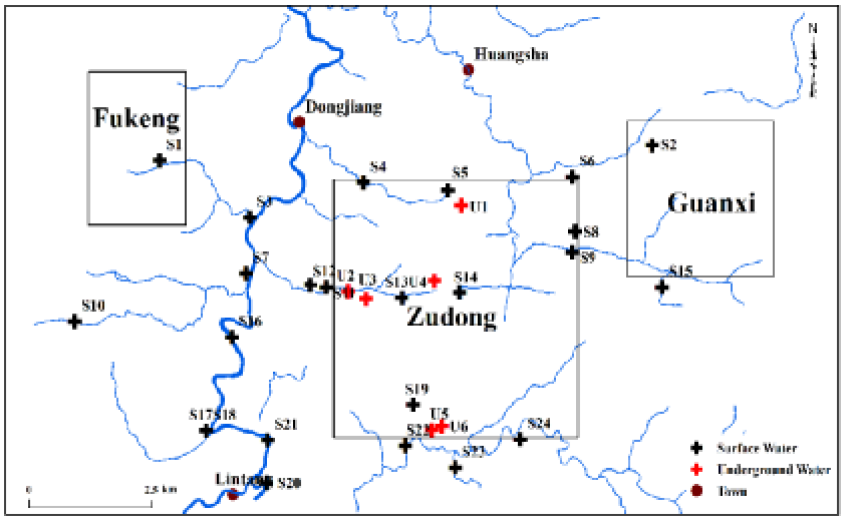

Fig 1 location of the sampling sites

1.2 EEM measurement

The samples were diluted with Milli-Q water prior to fluorescence analysis if absorbance values were higher than 0.04 (1 cm quartz cell, 254nm) to minimize inner filter effects[43,44,45]. Fluorescence EEMs were measured on a Hitachi F-7000 fluorescence spectrophotometer with a xenon lamp, creating high-resolution fluorescence running with band width slits of 5 nm for both excitation and emission. The scanning ranges were 220–420 nm for excitation and 250–550 nm for emission. Fluorescence readings were collected at intervals of 5-nm excitation with 2-nm emission wavelengths using a scanning speed of 1200 nm▪min^{-1}.

2 PARAFAC Modeling

In this study, PARAFAC was applied to DOM fluorescence EEMs and component analysis using MATLAB with the DOMFluor toolbox. Excitation emission matrix scans(EEMs) for a total of 30 samples were obtained by collecting a series of emission wavelengths ranging from 250nm to 550nm and excitation wavelengths ranging from 220nm to 420nm. The data in the region influenced by first order scatter(where Rayleigh and Raman peaks dominate the signal) and the region where emission wavelength was less than excitation wavelength should be cut and replaced with missing values or zeros. To reduce the Rayleigh scatter, data measured at emission wavelength between excitation wavelength-5nm and excitation wavelength+5nm were eliminated. After removing the Rayleigh and Raman scatters, non-negativity constraint was applied to the model, and all the loadings and leverages appeared to be more logical. Then EvalModel function was used to create a series of graphs including measured, modeled and residual EEM(Fig.2). Through Split Half analysis and validation process, the data were divided into two halves of similar curves and fit models with 3 to 7 components. Except a three component model, others could not be split-half validated. Thus, a three component model was confirmed to be adequate for split-half validation and capable of characterizing DOM of surface and underground water from Jiangxi Ore District. To create surface or contour plots of each component, the Component EEM or ComponentSurf functions could be used.

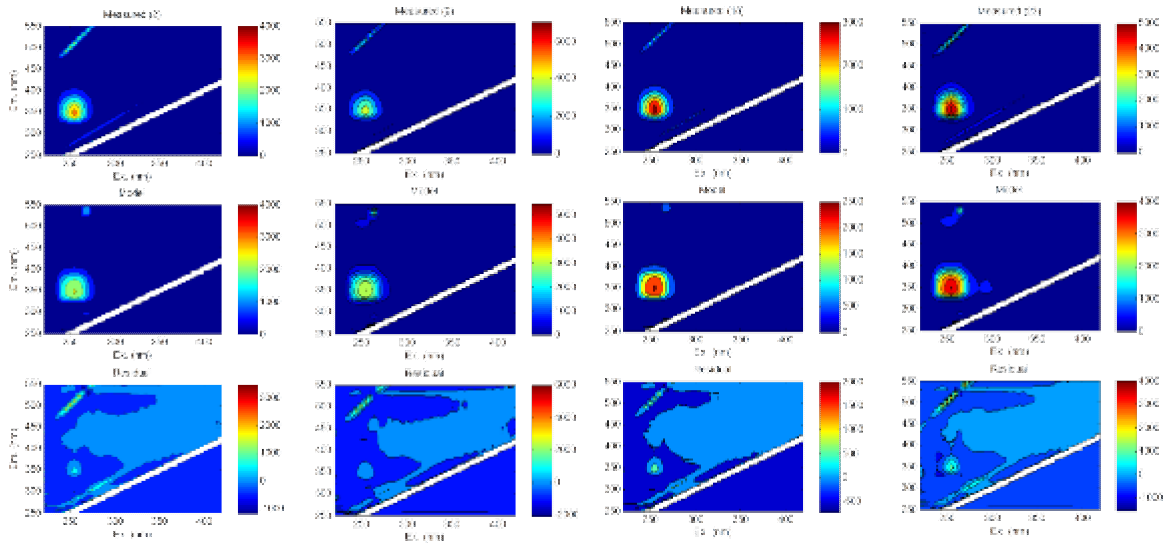

Fig 2. Examples of measured, modeled and residual EEMs for sample collected from sites of S2(2), S8(9), S14(18), S19(23). Fluorescence is shown in Raman Units (R.U.nm^{-1}).

3. Results and discussion

3.1 Fluorescence Characterization and PARAFAC analysis of EEM spectra

The spectral characteristics of three identified components were presented as a function of excitation and emission wavelength, and the fluorescence excitation and emission matrix spectra for three components and corresponding contour plots were shown in Fig 3. As shown in Fig 2, the PARAFAC model identified two protein-like substances(component 1 and component 2) and one humic-like substance(component 3). These components of DOM were confirmed by comparing the excitation/emission characteristic peaks with reported characteristic wavelength of pure substances. For instance, the major peaks of tyrosine and trytophan were usually detected at Ex/Em=275/310nm and 278/340nm[46], respectively, which were similar to the characteristic peaks of C1(270/310nm) and C2(251/352nm) in our study, thus C1 and C2 were confirmed as tyrosine-like and trytophan-like substance, separately. Similarly, C3 had Ex/Em characteristics(240, 272/460nm) close to those of fulvic or humic acid whose major peaks were detected at Ex/Em=240-270/430-462nm in freshwater rivers [47]. Consequently, C3 was identified as humic-like substance.

C1 had excitation/emission characteristics close to tyrosine(275/310nm)[46], which was related to bacteria degradation of organic material in waters and identified as autochthonous protein-like substances in earlier studies[29,48,49,50]. Characterized by peaks of excitation/emission 251nm/352nm, C2 had Ex/Em spectral characteristics similar to that of free amino acids or protein-bound amino acids (component 6) reported by Kowalczuk[51], which assumably represented a fluorescent tryptophan derived from autochthonous DOM. It was observed that the single excitation peak of C2 was blue shifted, while the emission peak was red shifted compared to the spectral characteristics of pure tryptophan, indicating that trytophan was bound into larger structures of organic molecules instead of pure compounds diluted in the water. According to previous studies, the presence of hydroxyl, alkoxyl, amino groups and carboxyl components might accounted for a slight red shift of emission peaks[52,53]. Susann[54]observed a shift towards smaller molecules in the molecular size distribution of DOM during incorporation to sea ice, with the

fluorescence intensity increasing at shorter emission wavelengths, which supposed that a longer emission wavelength for C2 might explain the shift towards larger molecules binding to DOM. However, additional detailed molecular knowledge is required to characterize DOM in Jiangxi region.

The fluorescence spectrum of C3 was similar to that of terrestrial humic-like substances identified by Yamashita[55]. C3 had a primary and secondary excitation peak at 240nm and 272nm, respectively, and a single emission peak around 460nm, which were similar to those peaks of humic-like PARAFAC components in previous studies[29,55,56,57]. These fluorophores have also been found in the EEM spectra exhibited by Zeri[50], which suggested the presence of humic-like component in coastal environments.

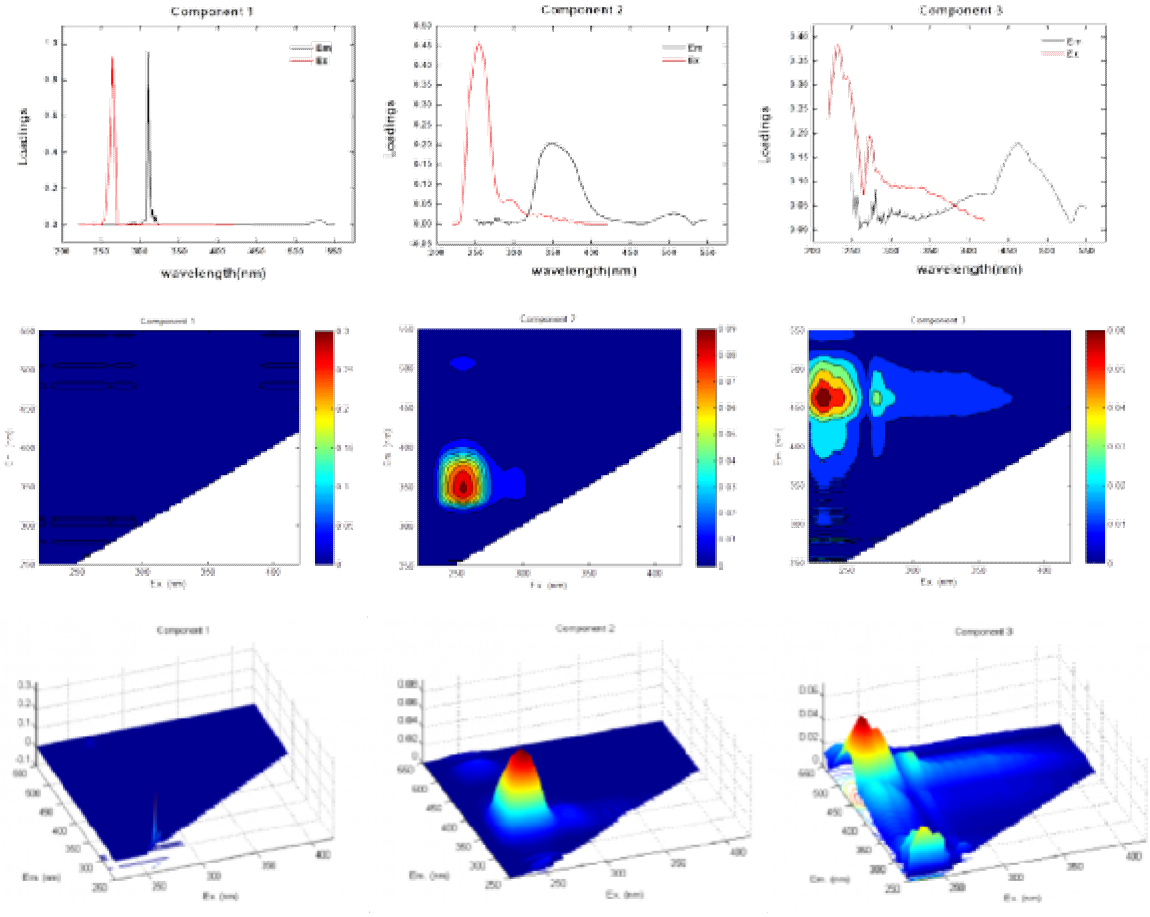

Fig 3. Excitation and emission loadings for the three different fluorescent components, and contour plots identified by PARAFAC model. Intensity is shown as Fmax in Raman Units(nm^{-1})

3.2 Distribution of DOM components in Longnan Ore District.

PARAFAC analysis provided quantitative information of DOM fluorescence composition concerning the distribution of three components for 30 samples collected at different stations. The humic-like substance represented by C3 accounted for the vast majority proportion in the composition of DOMs. As illustrated in Fig 4, C3 in S3 and S5, which were located in the west of sampling area, constituting 98.3% and 97.6% of the total compound for each sample, respectively, and C3 in S2 and S14 acquired from the eastern area took up 96.6% and 94.4%, with protein-like substance(component 2) occupying approximately 3% and 5% for each sample. The

tryptophan-like compounds(C2) of S1 substantially exceeded tryptophan content of other samples, which was probably input from the bank of downstream locations. Similarly, the protein-like substance tyrosine (component 1) accounted for merely a tiny fraction(<1%) in DOMs for all the samples, indicating that it was typically generated by biological processes in the stream or the surrounding environment. Based on the particular basin terrain of Jiangxi Ore district, the DOMs of surface or underground water in the middle such as S8, S9, S11, S12, S13, S22, S23, S24, U6 and U1, were basically higher than those surrounding the center(S2, S4, S5, S7, S15), indicating a higher content of protein-like and humic-like substances. However, downstream S18 and S20, located in the southwest of the ore district, were considered to be an exception which had higher DOMs values, revealing that sources of downstream could be traced back to upstream waters thus the downstream waters exhibited fairly high DOM content. S11 and S12 located in the tributary shared almost the same DOM value with underground water U2 and U3 in the neighboring sampling station, indicating a terrestrial source for S11 and S12 instead of an upstream runoff input. Whereas, S13 as the downstream of tributary, presented a significantly higher DOM value not only than S11 and S12, but also than the underground water U4 in the vicinity, showing a consequence of upstream and terrestrial source. S4 and S5 followed the same trend of DOM content as S12 and S13, while the remarkably higher DOM value of U1 could explain the source of S5 was generally released from upstream rather than terrestrial source. The distribution of components showed minor variations of DOM between stations S19, S22, S23, S24, U5 and U6, which testified a homologous source of DOMs for samples in the southern area. The surface water samples S2 and S15 collected at almost the same longitude had similar fluorescence intensities, which were lower than those of S6, S8, S9 taken in the same longitudinal zone due to its relatively high elevation as well as the upstream topography.

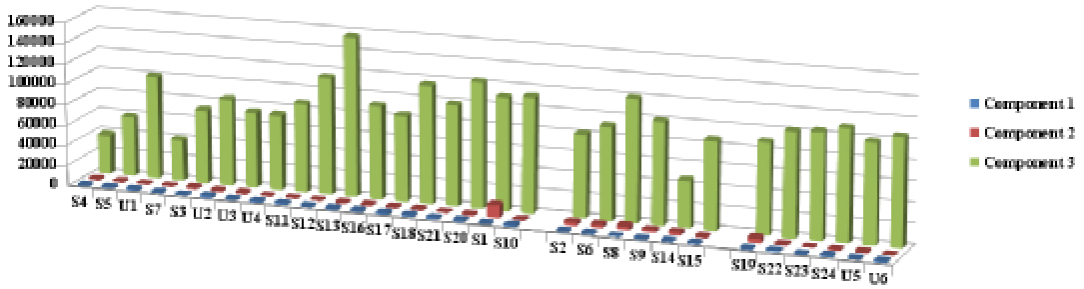

Fig 4 Distribution of three PARAFAC-identified components in DOMs at selected sampling stations. Bar plots indicated the fluorescence intensities of three components for each sample collected at different districts.

3.3 **Behavior of PARAFAC-derived components with changes of pH and concentrations of metals.**

A negative linear correlation (R^2=0.8465) between fluorescent C3 and pH (5.7~9.2) were observed in Fig 5, suggesting that fluorescence intensities of humic-like substances were influenced by changes in pH, whereas the other two components were basically unrelated to pH condition. Dissolved humic substances of DOM was strongly pH-dependence with humic acid soluble at pH>2 and fulvic acid soluble at all pH values, and the fraction of dissolved humics would increase with increasing pH[58], in contradict with the results showing a negative relation

between pH and fluorescence intensities of humic-like component in our report. Therefore there might be other reasons, such as DOM-metal coordination, or the change of molecular weight of components caused by pH change, leading to this phenomenon. According to the results reported by Pourret[42], the amount of REE bound to humic acid strongly increased with increasing pH, indicating that a higher pH stimulates the complexation of REE and humic substances, which might reduce the concentration of humic substances with impairing fluorescence intensities. The conclusion drawn by Chen[59] also confirmed that pH was the key water chemistry parameter to regulate DOM binding to metal ions, since the binding affinity to Cu^{2+} of Suwannee River fulvic acid was remarkably suppressed when lowing pH from 6 to 4, thus consequently causing an increase of DOM fluorescence intensity in water samples. In addition, the findings that the molecular weights of DOM increased gradually with pH values ranging from 10.5 to 2.5[60], were consistent with the results suggesting higher molecular sizes occur with lower pH values[61], providing a possible explanation for negative correlation between pH and fluorescence intensity of DOM if the molecular weights of DOM fraction were proved to be positively associated with its fluorescence intensity. However, the pH values in the middle area of the ore district remained stable around 7.0, and the underground water samples (U5, U6) from southern area were slightly acidic with pH around 6.5, while the surface water samples nearby(S21-S24) were alkaline with pH ranging from 8.3 to 9.5, indicating that the composition of surface water were assumedly irrelevant to terrestrial origin.

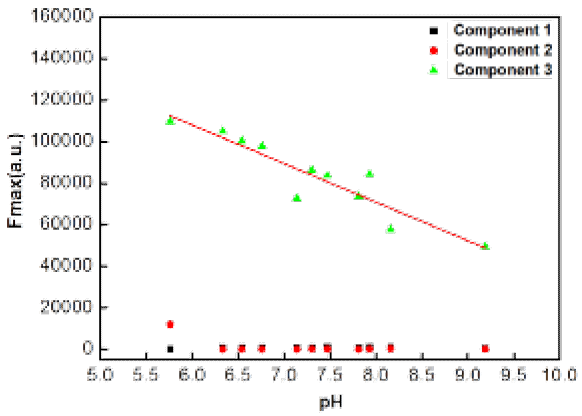

Fig 5 A linear correlation between fuorescence intensity and pH for three components

Recent studies have demonstrated that PARAFAC-EEM quenching could be employed to investigate the interactions between metal ions and fluorescent components of DOM from soil and water samples[14,62,63,64]. Therefore, apart from pH values, the fluorescence quenching effects of metals also played a significant role in affecting the fluorescence properties of different components identified by the PARAFAC model in EEMs of samples of surface and underground waters in the Jiangxi Ore District.

As illustrated in Fig 6, a significant quenching of fluorescence intensity of C1 (tyrosine-like substances) were observed in the presence of cobalt(Co), nickel(Ni), uranium(U), Th and several rare earth elements such as La, Nd, Ce, Pr, Gd, Dy, etc. It was interesting to find that the quenching effects of Co and Ni were strong for C1, whereas they were weak for C2, however, the presence of copper(Cu) and titanium(Ti) slightly quenched the fluorescence intensity of C2

(trytophan-like material) instead of C1, reflecting that tyrosine-like substances contributed to Co/Ni complexation, while Cu/Ti binding was induced by trytophan-like compound. Obviously, strong quenching effects of heavy metals were mostly exhibited in C1 instead of C2 even both of them were identified as protein-like components by PARAFAC model, indicating that tyrosine-like materials were presumably responsible for metal binding in DOM, thus producing non-fluorescent compounds that led to quenching effect, which was consistent with previously published results describing the quenching effects of heavy metals on fluorescent protein-like components of DOM as a consequence of complexation of metal ions[14][65].

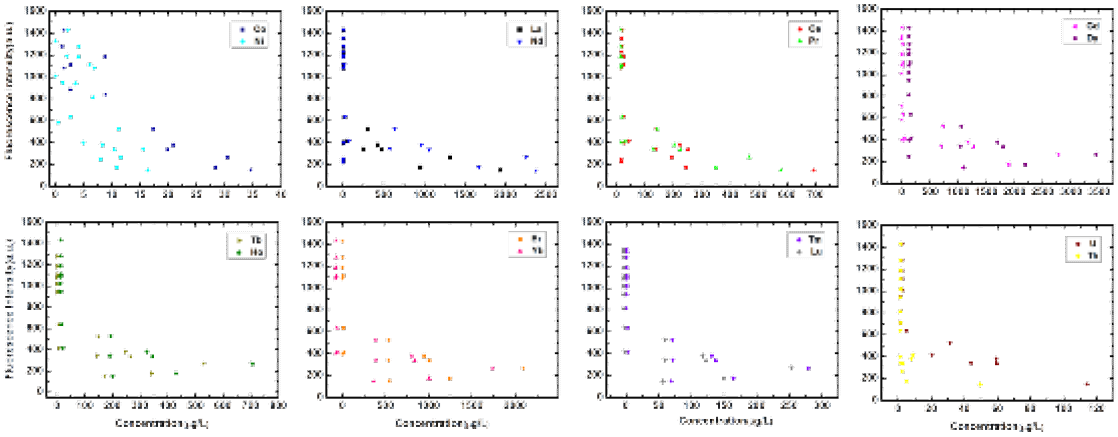

Fig 6 Changes in the fluorescence intensity of component 1 with the increase of concentrations of Co, Ni and some rare earth metals

A positive correlation between C2 and concentrations of various metals were observed with the fitting linear equations shown in Fig 7. We could see that concentrations of most of the lanthanides, Y and radioactive element U increased linearly with the increase of the fluorescence intensity of C2, suggesting that the component of DOM sycophant, due to its high molecular weight, hydrophobicity and aromatic functional groups[32], might have a positive impact on the adsorption of rare earth metals such as La, Ce, Nd, Sm, Tb, Dy, Ho, Yb, Y, etc, which could be used as an indicator to evaluate the capacity of rare earth metal absorption of underground and surface water in Jiangxi Longnan Ore District. Previous studies indicated that the dominant control on rare earth metal-DOM complexation, was rare earth elements binding to weak sites on DOM with relatively high molecular weight in natural terrestrial waters[66,67].Moreover, a consistent trend of Tm/Lu and Er/Yb displayed in concentration changes with fluorescence intensity, revealing the process of coadsorption of heavy rare earth elements on DOM in surface water samples.

Yet, despite the fluorescence intensity curves of C3 with concentration changes of U/Th, Gd/Dy, Tb/Ho, Tm/Lu and Er/Yb had a similar tendency, there was neither distinct correlation observed between fluorescence intensity and metal concentration, nor quenching effect shown in a wide range of metal concentrations, thus indicating that humic-like component was likely to absorb some metals in a considerably narrow concentration range, but in general irrelevant to the formation of new complex coordinated with rare earth elements such as Tm, Yb and Er. In a study conducted by Motoki[68], a similar ideas might explain the reason, which proposed that the humic-like substances in the DOM of Horonobe groundwater had a lower binding affinity for lanthanides and actinides. Whereas, the interaction between dissolved rare earth metals and humic

acids was described in some studies[69,70], which discussed the influence of humic acid on the complexation behavior of lanthanides.

Recently, heavy metal pollution of soil, water and sediment has become a hot issue, which focuses on modes of occurrence, migration of heavy metal pollutants and biotoxicity in the field of environmental monitoring. DOM can strongly affect metal speciation and the formation of metal-DOM complexes may alleviate the harm from dissolved metals in soil, water and sediment[67][71]. However, due to the high complexity of components of DOM, not only the influence of DOM on the behavior of heavy metals in soil, water and sediment remains to be investigated, but the internal mechanism for the migration and absorption of heavy metals also requires a further explanation, thus making DOM as an indicator to assess heavy metal chelation and migration effects.

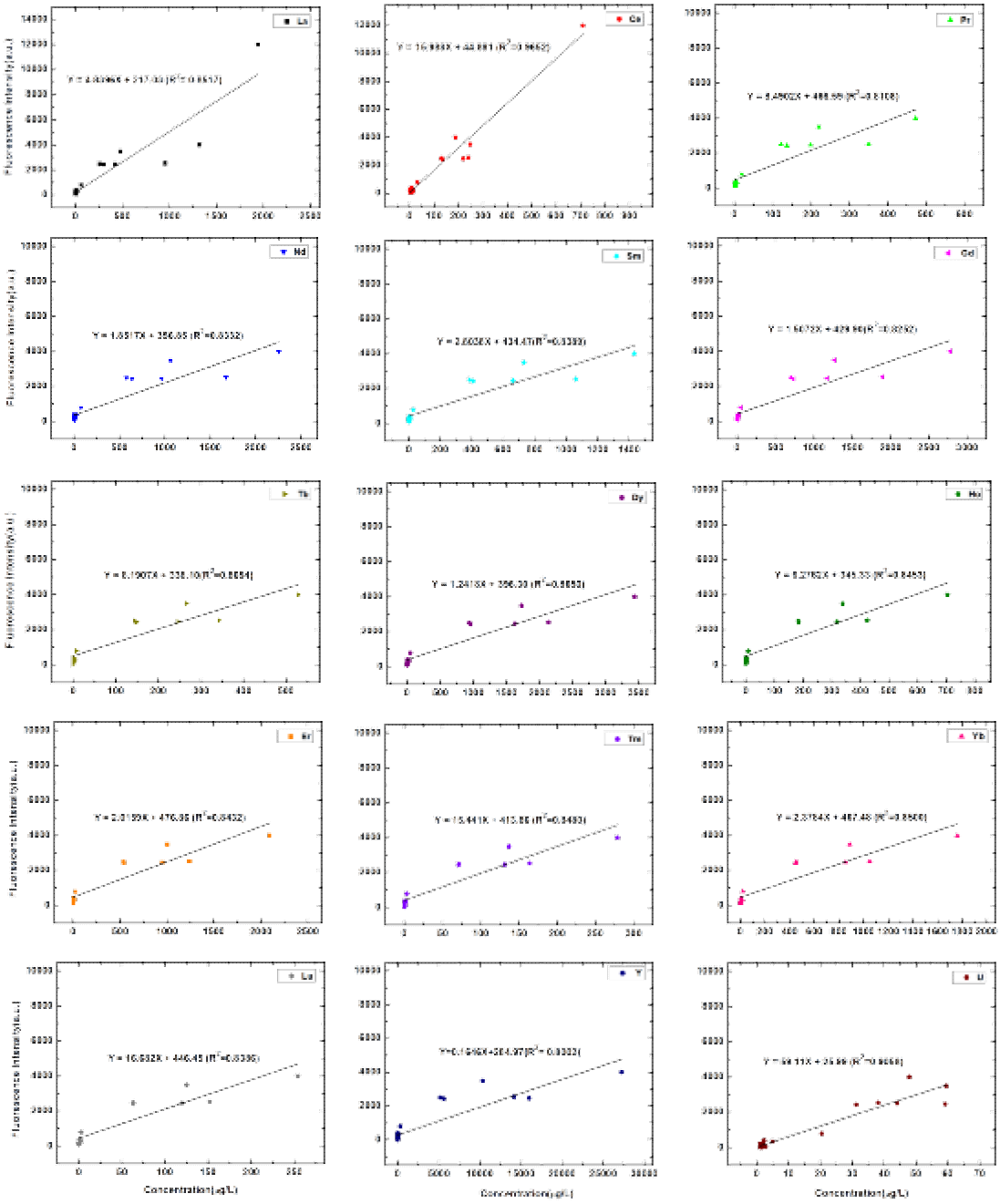

Fig 7 Relationship between concentration of various rare earth metals and fluorescence intensity of component 2.

316

317 # 4 Conclusion

318 This study provides information on DOM components of water samples from Jiangxi
319 Longnan Ore District with the following conclusions drawn on the basis of EEM-PARAFAC
320 analysis: (1) Two protein-like substances(C1 and C2) and one humic-like substance(C3) were
321 identified by PARAFAC model. (2) Due to the influence of river flow direction and terrain, the
322 fluorescence intensity of DOM components from downstream or in central region was relatively
323 higher than that from upstream or surrounding the center. (3) Linear decrease in fluorescence

intensity of C3 with the increase of pH was observed, while C1 and C2 was not affected by pH condition. (4) The quenching effect and linear correlation between protein-like components and rare earth metals accounted for the metal-DOM complexation and adsorption in water samples. Results from our study have considerable implications for the role of DOM components on the toxicity and migration behavior of rare earth metals, and the mechanism of pollutant adsorption and desorption by organic matter under unique geological settings. Furthermore, it shows excellent predictions on main chemical structure of organic matter, and critical control factors based on the capacity and strength of DOM affecting the complexation or adsorption with toxic metals.

Acknowledgments

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Figure Captions

Fig 1. location of the sampling sites

Fig 2. Examples of measured, modeled and residual EEMs for sample collected from sites of S2(2), S8(9), S14(18), S19(23). Fluorescence is shown in Raman Units (R.U.nm^{-1})

Fig3. Excitation and emission loadings for the three different fluorescent components, and contour plots identified by PARAFAC model. Intensity is shown as Fmax in Raman Units(nm^{-1})

Fig 4. Distribution of three PARAFAC-identified components in DOMs at selected sampling stations. Bar plots indicated the fluorescence intensities of three components for each sample collected at different districts

Fig 5. A linear correlation between fuorescence intensity and pH for three component

Fig 6. Changes in the fluorescence intensity of component 1 with the increase of concentrations of Co, Ni and some rare earth metals

Fig 7. Relationship between concentration of various rare earth metals and fluorescence intensity of component 2

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